

# A Comparative Study on Sulfonated PEEK and PVDF Blend Membranes for Direct Methanol Fuel Cells

Göknur Dönmez and Hüseyin Deligöz\*

*Istanbul University, Engineering Faculty, Department of Chemical Engineering, 34320 Avcılar, Istanbul, Turkey*

**Abstract:** Various polymeric blend membranes based on sulfonated poly(ether ether ketone) (sPEEK) and poly(vinylidene fluoride) (PVDF) are prepared by solution casting method for direct methanol fuel cells (DMFCs). Physicochemical properties of the membranes are studied after blending sPEEK with PVDF in different ratios. It is found that the thermal stabilities of all blend membranes are above 200°C which is sufficiently high for use in DMFC. Water uptake values of the blend membranes vary between 9-20% as a function of the blend composition. Similar to the water uptake property, proton conductivity values and surface hydrophilicity of the samples increase with sPEEK portion in the blend. Water uptake of sPEEK30/PVDF70 blend membrane is about 9.2%, the proton conductivity of this membrane is 0.8 mS.cm<sup>-1</sup>, and the methanol permeability of sPEEK30/PVDF70 blend membrane is about 1/10 that of untreated Nafion®117 reported in the literature. Based on the results, it is concluded that the sPEEK/PVDF polymer blends can be considered as a candidate membrane for DMFC applications considering their controllable properties, cheapness and easy preparation.

**Keywords:** Blend membranes, Direct methanol fuel cell, Electrolyte, PVDF, sPEEK.

## 1. INTRODUCTION

Nowadays, the generation of clean, efficient and environmental-friendly energy is one of the major challenges for engineers and scientists. Fuel cells convert the chemical energy of a fuel gas directly into electrical energy. They are efficient and environmentally clean without combustion. Fuel cell systems are available to meet the needs of applications ranging from portable electronic devices to utility power plants. Promising applications for fuel cells include portable power, transportation, building co-generation and distributed power for utilities [1].

Among the several types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have gained considerable attention as promising systems for portable applications [2-4]. In general, hydrogen is used as fuel in polymer electrolyte membrane fuel cells. Due to the disadvantages associated with hydrogen (e.g. absence in nature, obtaining with a chemical process, storage problem, operating safety), liquid fuels come into prominence. Direct methanol fuel cell (DMFC), using liquid methanol fuel, is a favorable option compared to hydrogen-fed fuel cells. The major limitation of the commercially available perfluorosulfonated membranes in DMFCs is that they exhibit high methanol permeability ( $P_M$ ) from anode to cathode leading a reduction in the electrical performance [5-7], although they offer numerous

benefits, such as high efficiency, high power density and low or zero emissions. Therefore, some approaches were reported for suppressing methanol diffusion through the electrolyte. The first one is the modification of fluorinated and non-fluorinated membranes with the addition of inorganic components [8-13]. This attempt dramatically reduced  $P_M$  with slightly sacrificing proton conductivity ( $\sigma$ ). Recently conductive polymers, polyaniline (PANI), polypyrrole (PPy) and polybenzimidazole (PBI) were also introduced into Nafion to barrier the methanol transport [14-17]. In an alternative approach, various multilayered composite membranes were studied and it was reported that the methanol permittivity decreased due to the formation of thick barrier film on Nafion membrane [18, 19].

Among the polymers studied in the literature, sPEEK is considered one of the most promising and alternative option for fabrication of membranes to be used as an electrolyte in DMFCs [20]. sPEEK has many advantages, such as low cost, easy sulfonation process, low methanol permeability and high proton conductivity at a high degree of sulfonation [21]. In spite of its various benefits, sPEEK must be modified to improve the membrane properties. Hence, polymer blending is considered as a cost-effective method for the modification of sPEEK [22]. There are several works on blending of sPEEK with poly(ether sulfone) [23], poly(ether imide) [24] and polysulphone [25,26]. Blending of sPEEK with PVDF is one of the important methods discussed in the literature because PVDF is mechanically tough and resistant to methanol

\*Address correspondence to this author at the Department of Chemical Engineering, Istanbul University, 34320 Avcılar, Istanbul, Turkey; Tel: 90-212-473 70 70/17758; E-mail: [hdeligoz@istanbul.edu.tr](mailto:hdeligoz@istanbul.edu.tr)

crossover [27-29]. In a very fresh article, novel blend membranes of poly(vinylidene fluoride) grafted poly(styrene sulfonic acid) (PVDF-g-PSSA) with sPEEK were prepared for DMFC applications to disperse PVDF-g-PSSA in the sPEEK matrix homogeneously [30]. As we know, sPEEK has hydrophilic domains and methanol diffuses primarily through the hydrophilic water-rich domains. In this study, it was aimed to compensate these hydrophilic domains by formation of blend structure with PVDF due to its hydrophobic nature and to find a membrane with optimum proton conductivity ( $\sigma$ ), suppressed methanol permittivity ( $P_M$ ) and dimensional stability. Furthermore, the effects of sPEEK content on methanol permeability, proton conductivity, membrane selectivity ( $\Phi$ ) and morphology of the blend membranes were investigated comparatively.

## 2. MATERIALS AND METHODS:

### Chemicals and Materials

PEEK extruded pellets were provided by Polysciences, Inc. and PVDF (Molecular weight: average  $M_n \sim 71000$ , average  $M_w \sim 180000$  by GPC) were provided by Sigma-Aldrich. Sulfuric acid (95-98 wt%, Sigma-Aldrich), dimethylacetamide (DMAc, Merck), N-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich) and methanol (Sigma-Aldrich) were also used as received. Milli-Q-water ( $R=18.2 \text{ M } \Omega$ ) was used for all preparation and analysis experiments.

### Sulfonation of PEEK

Sulfonation of PEEK was carried out as reported in a previous study [31]. 5 g of PEEK was dissolved in 250 mL of concentrated sulfuric acid and stirred vigorously at room temperature until completely

dissolved. After sulfonation process was completed, the sulfonated polymer was recovered by precipitating the solution into a large excess of ice water. The polymer suspension was left to settle overnight. The precipitate was filtered, washed until pH was neutral. After washing, the precipitate was dried under vacuum for 12 h at  $90^\circ\text{C}$  and finally it was ground. The obtained yellowish powder was called as sulfonated poly(ether ether ketone) (sPEEK).

### Preparation of the Blend Membranes

Blend membranes were prepared using 10% wt. solution of sPEEK dissolved in NMP and 10% wt. solution of PVDF dissolved in DMAc at five different compositions (sPEEK/PVDF, 50/50, 45/55, 40/60, 30/70, 25/75 in volume). The obtained membranes were abbreviated as sPEEK(X)-PVDF(Y), where X and Y indicate the volumetric percent of sPEEK and PVDF solutions in the blend composition. After blending and pouring into a Teflon mold, the solutions were left overnight for degassing. Finally, the membranes were dried in an oven at  $80^\circ\text{C}$  and  $100^\circ\text{C}$  for 1 h and  $120^\circ\text{C}$  for 3 h. Pictures of the sPEEK membrane preparation steps are shown in Figure 1. In addition to the blend membranes, pure sPEEK and PVDF membranes were also prepared to compare the results.

### Characterization

Thermal behavior of the membranes was studied with an SII Exstar 6000 thermogravimetric/differential thermal analysis (TG/DTA) 6300 between  $40\text{-}600^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}.\text{min}^{-1}$  under air atmosphere. Proton conductivities ( $\sigma$ ) of the blend and pure membranes were measured by two-probe method using a Solartron 1260 Frequency Response Analyzer



**Figure 1:** Pictures of (a) PEEK in sulfuric acid solution, (b) precipitated sPEEK in Milli-Q water, (c) dried and powdered sPEEK and (d) sPEEK film in a Teflon mould.

(FRA) and Solartron 1296 Dielectric Interface. The membrane was cut in 2 cmx2.5 cm dimensions and impedance measurements were performed in water at  $22\pm1^\circ\text{C}$ . Impedance measurements were performed in water with a test system described in our previous paper [32]. The proton conductivity was calculated from Eq. (1).

$$\sigma = \frac{L}{RA_d} \quad (1)$$

where  $\sigma$  is the proton conductivity,  $L$  is the distance between Pt electrodes,  $d$  is the thickness of the membrane,  $R$  is the bulk resistance value measured.

Water uptake values were determined according to the procedure used in a study [33]. All membranes were conditioned at  $105^\circ\text{C}$  for 1 h and then  $50^\circ\text{C}$  for 24 h at an oven. Samples were cooled to room temperature and immediately weighted ( $W_{\text{dry}}$ ), and then immersed in water at room temperature for 24 h. The membranes were removed from water and weighted again ( $W_{\text{wet}}$ ). Water uptake values of the blend and pure membranes were calculated as follows [33]:

$$WU(\%) = 100 \times \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \quad (2)$$

Methanol permeation measurements of the membranes were carried out using a U-shaped home-made apparatus which consists of two different compartments filled with ultra-pure Milli-Q water and 10 M of methanol solution. Methanol concentration diffused through the membrane was detected with time using a Zeissler refractive indexer. Methanol concentration in Milli-Q water compartment was significantly increased and then reached a plateau over 30 h. Therefore, all methanol permeation tests were carried out during this time. Methanol permittivity values of the membranes were calculated using Eq. (3).

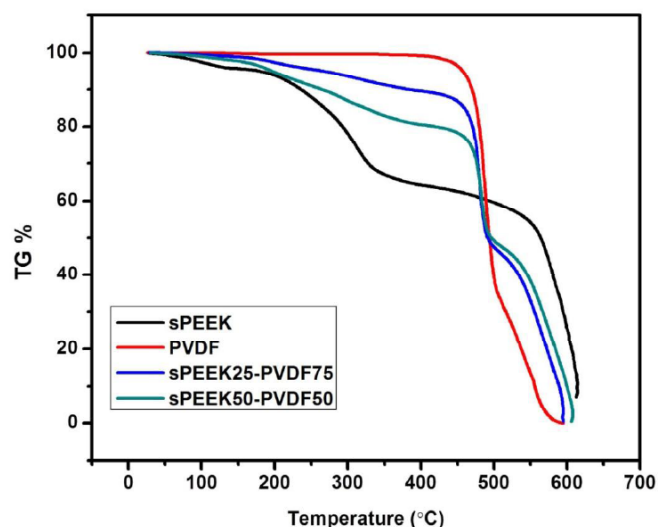
$$C_{B(t)} = \frac{A \cdot C_{A0} \cdot (t - t_0)}{V_B \cdot L} \cdot P \quad (3)$$

Where  $C_{B(t)}$  is the methanol concentration diffused through membrane at any time,  $A$  is the area of membrane,  $C_{A0}$  is the concentration of methanol solution (10 M),  $V_B$  is the volume of liquid in pure water part of apparatus,  $L$  is the membrane thickness and  $P$  is the methanol permittivity of membrane.

Contact angle measurements of the blend and pure membranes were performed using KSV Attension Tensiometer. The contact angles presented here are static contact angles measured with the standard pendant drop technique and volume of the water droplet was maintained constant at 5  $\mu\text{L}$ . The measurements were repeated three times for each sample. Morphology of all prepared membranes and the phase distribution in blend membranes were observed using Field Emission Scanning Electron Microscopy (FESEM). For SEM analysis, the samples broken after cooling in liquid nitrogen were sputtered with gold and measured by a FEI Quanta FEG instrument at an operation voltage of 10 kV. Also energy dispersive X-ray analysis (EDX) provided an elemental analysis of the samples.

### 3. RESULTS AND DISCUSSION

Thermal gravimetric analysis (TGA) plots of the pure and blend membranes, namely sPEEK25/PVDF75 and sPEEK50/PVDF50, are shown in Figure 2. While pure PVDF had one thermal degradation step starting from  $450^\circ\text{C}$ , sPEEK exhibited thermal degradation in three regions. Similarly thermal decompositions of the prepared blend membranes occurred in three steps and all blend membranes showed the similar TG patterns. The initial weight loss is related to the removal of water adsorbed on the sample. The second transition in the temperature range of  $200\text{--}450^\circ\text{C}$  is attributed to a loss of sulfonic acid groups in sPEEK. The third loss occurred between  $450$  and  $500^\circ\text{C}$  can be ascribed to the decomposition of sPEEK and PVDF backbone. Regarding the comparison of thermal degradation of blend membranes with 25 and 50 percent of sPEEK, they exhibited nearly the same TG patterns. The blend membrane with 75 percent of PVDF showed slightly higher thermal stability than that of the membrane with lower amount of PVDF in the blend composition. This result can be directly attributed to the presence of thermally labile sulfonic acid groups in higher proportions. Another reason may be the lower water uptake of the blend membrane with high PVDF content. On the other hand, thermal degradation onset temperatures of the blend membranes were roughly above  $200^\circ\text{C}$ . It meant that all prepared sPEEK/PVDF membranes were stable at DMFC operation temperature and their thermal stabilities were high to meet the requirements of DMFC.



**Figure 2:** Thermogravimetric (TG) patterns of the pure PVDF (red line), pure sPEEK (black line), sPEEK25/ PVDF75 (blue line) and sPEEK50/PVDF50 (green line).

Table 1 shows and compares the proton conductivity ( $\sigma$ ), water uptake, methanol permittivity ( $P_M$ ) and membrane selectivity ( $\Phi$ ) of the membranes and Nafion®117 reported in the literature. The proton conductivity of pure sPEEK membrane is  $8.6 \text{ mS.cm}^{-1}$  and comparable to Nafion®117 membrane's proton conductivity value [34]. When sPEEK was blended with PVDF at different ratios, proton conductivity values of the blend membrane raised with sPEEK in the blend composition and  $\sigma$  reached to  $2.24 \text{ mS.cm}^{-1}$  for sPEEK50/PVDF50. This expected increase in conductivity can be attributed to the presence of relatively high proportion of proton carrier sulfonic groups in the blend membrane. Also, improvement in water uptake properties of the blend membranes

containing higher amount of sPEEK can lead to facilitate the proton transport through the polymer electrolyte membrane. Similar to  $\sigma$  results, water uptake of the blend membrane increased with sPEEK proportion in the blend. Water uptake of the pure sPEEK membrane was found to be 44.9%. As expected, water uptake of the pure sPEEK membrane quite high when compared with the pure PVDF membrane (1.6%) due to their hydrophilic/hydrophobic nature. Furthermore, we observed similar trends in water uptake values of the blend membranes. Although the blend membranes with low sPEEK content had very small water uptake, the value reached to 20% with fifty percent of sPEEK in the blend. In a study, water uptake value for pure sPEEK membrane was found of 30% and it was reported that this result was very close to literature value of sPEEK [30, 35]. In general, high water uptake is a prerequisite for a good proton-conducting membrane because water would induce a dissociation of the protons from sulfonic groups and would also act as "vehicles" for the transportation of the protons from the anode to the cathode [30, 36]. On the other hand, most proton-conducting membranes based on sulfonated aromatic polymers exhibit significant dimensional change by hydration, and this leads to degradation of fuel cell performance on a prolonged operation. Because of these reasons, it was considered that the blend membranes with 30-50% sPEEK content are suitable for DMFCs in conjunction with conductivity and water uptake properties.

Besides, preliminary methanol permeation results are shown in Table 1. High methanol crossover through the ionic conducting polymer membrane is a very important problem to be overcome for DMFC

**Table 1: Proton Conductivity ( $\sigma$ ), Water Uptake %, Methanol Permivity ( $P_M$ ) and Membrane Selectivity ( $\Phi$ ) of the Pure and Blend Membranes**

Membrane Code	Proton Conductivity ( $\sigma$ ) ( $\text{mS. cm}^{-1}$ )	Water Uptake %	Methanol Permivity ( $P_M$ ) ( $\text{cm}^2.\text{s}^{-1}$ )	( $\Phi$ ) <sup>a</sup> ( $\text{S.s.cm}^{-3}$ )
sPEEK	8.6	44.9	$2.23 \times 10^{-6}$	$3.86 \times 10^3$
PVDF	0.2	1.6	--	--
sPEEK50/PVDF50	2.24	20	n.d	--
sPEEK45/PVDF55	1.23	11.6	n.d	--
sPEEK40/PVDF60	1.14	9.6	n.d	--
sPEEK30/PVDF70	0.8	9.2	$6.53 \times 10^{-8}$	$1.22 \times 10^4$
sPEEK25/PVDF75	0.6	9.1	--	--
Untreated Nafion®117 <sup>b</sup>	37.8	--	$6.04 \times 10^{-7}$	$6.25 \times 10^4$

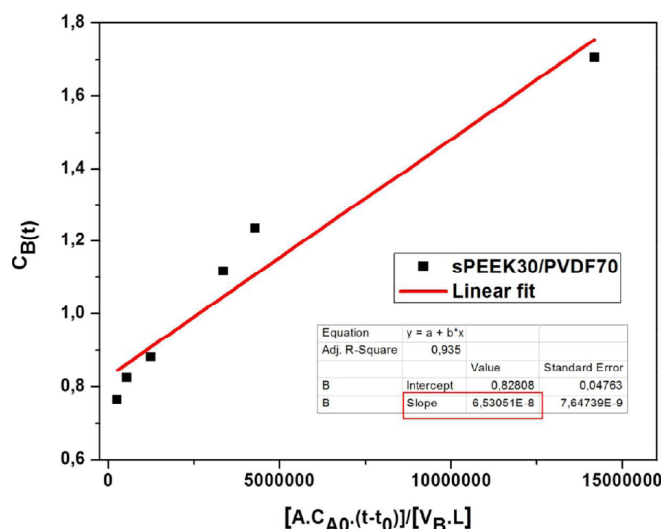
a: Membrane selectivity ( $\sigma/P_M$ ).

b: Ref.[34]

n.d.: Not detected due to insufficient mechanical integrity of the blend membranes during the methanol permeation tests.



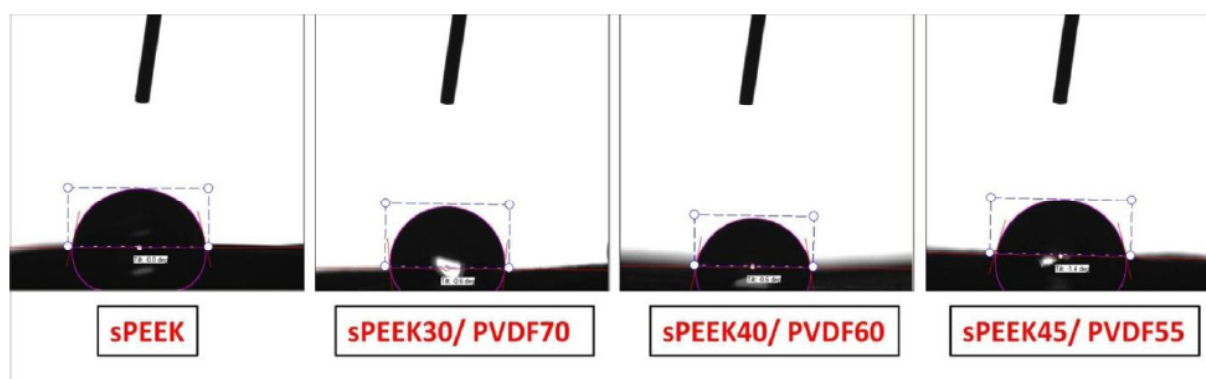
applications. In Nafion-based membranes, methanol diffusion rate and the proton conductivity are in a trade-off relationship with each other, *i.e.*, the membrane with higher proton conductivity shows higher alcohol crossover. As we know, sPEEK has hydrophilic domains and methanol diffuses primarily through the hydrophilic water-rich domains. Here, we tried to compensate these hydrophilic domains by formation of blend structure with PVDF due to its hydrophobic nature.  $P_M$  values of the membranes were determined by calculating the slope of Eq. 3 and the methanol permeability graph of sPEEK30/PVDF70 is given in Figure 3 as an example. One can see from Table 1 that the methanol permeabilities of sPEEK and sPEEK30/PVDF70 were determined as  $2.23 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$  and  $6.53 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ , respectively. These results showed that methanol permeability of the blend membrane significantly decreased with PVDF content and was much lower (roughly 35 times) than that of pure sPEEK, whereas proton conductivities of the membranes were comparable to that of pure sPEEK. This can be explained by the presence of PVDF which is in water-repelling (hydrophobic) nature in the blend composition. Another reason can be the formation of dense membrane structure via solution casting method. Comparing to Nafion<sup>®</sup>117 reported in the literature,  $P_M$  of the blend membrane was 10 times lower than that of Nafion<sup>®</sup>117, whereas proton conductivities of the commercial membrane was much larger to that of sPEEK/PVDF blend membrane [37]. On the other hand,  $P_M$  of the blend membranes with more than 30% of sPEEK could not be measured due to the insufficient mechanical integrity of the samples during the methanol permeation tests.



**Figure 3:** Methanol permeability of sPEEK30/PVDF70 membrane at room temperature.

Regarding the membrane selectivity, the selectivity factor ( $\Phi$ ) is defined as the ratio of proton conductivity to methanol permeability and used as an indicator of the suitability of a given membrane for DMFC applications. Table 1 shows  $\Phi$  of the pure sPEEK and sPEEK30/PVDF70 membranes comparatively. Also, Table 1 indicates the membrane selectivity of Nafion<sup>®</sup>117 reported in the literature.  $\Phi$  values of sPEEK and sPEEK30/PVDF70 were calculated as  $3.86 \times 10^3$  and  $1.22 \times 10^4 \text{ S} \cdot \text{s} \cdot \text{cm}^{-3}$ , respectively. These results indicated that the blending of sPEEK with PVDF led to an improvement in membrane selectivity of the blend membrane due to the significant enhancement in methanol barrier properties. On the other hand, membrane selectivity result of Nafion<sup>®</sup>117 in the literature was 5 times higher than that of sPEEK30/PVDF70. This lower selectivity for blend membrane can be attributed to its low proton conductivity. In conclusion, membrane selectivity of sPEEK30/PVDF70 blend membrane can be acceptable and this membrane can be considered as a good candidate due to its acceptable physical properties and dimensional stability for DMFC applications.

Contact angle ( $\theta$ ) measurements of the membranes were performed to observe the surface hydrophilicity. Contact angle measurements were repeated three times per sample and average results were calculated. The surface and droplet images obtained during measurement are shown in Figure 4 and contact angle values were given in Table 2. One can see from Table 2 that the average contact angle of sPEEK was  $76.5^\circ$  while  $\theta$  values of the blend films were found to be in the range of  $75.2$ – $94.6^\circ$ . Contact angles of the blend membranes increased with PVDF and contact angle of sPEEK30/PVDF70 reached to  $94.2^\circ$ , which is generally accepted as hydrophobic. On the other hand, sPEEK45/PVDF55 exhibited an average contact angle of  $75.2^\circ$  and it can be accepted as hydrophilic. This reduction in average contact angles of the blend membranes with higher amount of SPEEK can be mainly attributed to the hydrophilic nature of sulfonic acid groups. These results also confirmed the obtained water uptake and proton conductivity data. Interestingly, it would be expected that the lowest average contact angle for pure sPEEK. However, sPEEK45/PVDF55 showed slightly lower contact angle value than that of pure sPEEK. Probably, this slight difference can be explained by the morphology of the pure and blend membranes.



**Figure 4:** Contact angle measurement images of the pure sPEEK and some of blend membranes.

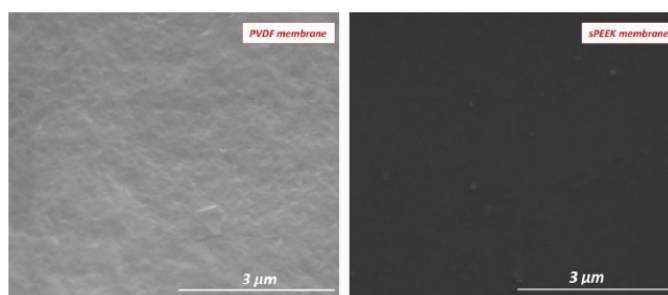
**Table 2:** Average Contact Angle Values of some of the Pure and Blend Membranes

Membrane Code	Contact Angles ( $\theta$ )		Average Contact Angles ( $\theta_{ave.}$ )
	Left	Right	
sPEEK	76.6	76.5	76.5
sPEEK30/PVDF70	95.4	93.8	94.6
sPEEK40/PVDF60	79.7	79.9	79.8
sPEEK45/PVDF55	74.5	75.9	75.2

SEM photographs of the pure and blend membranes were taken to observe the distribution of sPEEK in the PVDF matrix and morphology of the pure and blend membranes. Also, EDS graphs for blend

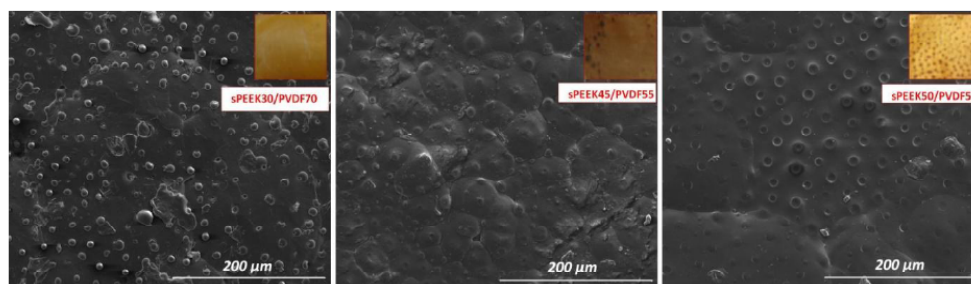
phases in sPEEK50/PVDF50 membrane are shown in Figure 6. As one can see from Figure 5 (a) and (b) that pure sPEEK and PVDF membranes were dense, uniform and defect-free. Regarding the surface and distribution of blend membranes, it can be clearly seen two different phases for the membranes with more than 30% of sPEEK. One of the phases is the main phase and the other one is spherically disturbed phase. With increasing sPEEK in the blend composition, aggregates of the some spherical formations were observed. This is probably due to the formation of some clusters of water-loving (hydrophilic) parts ( $-\text{SO}_3\text{H}$  groups) in the hydrophobic parts or vice versa.

Further, EDS analyses were performed to be sure about the phases and it can be seen from Figure 6 that



(a)

(b)

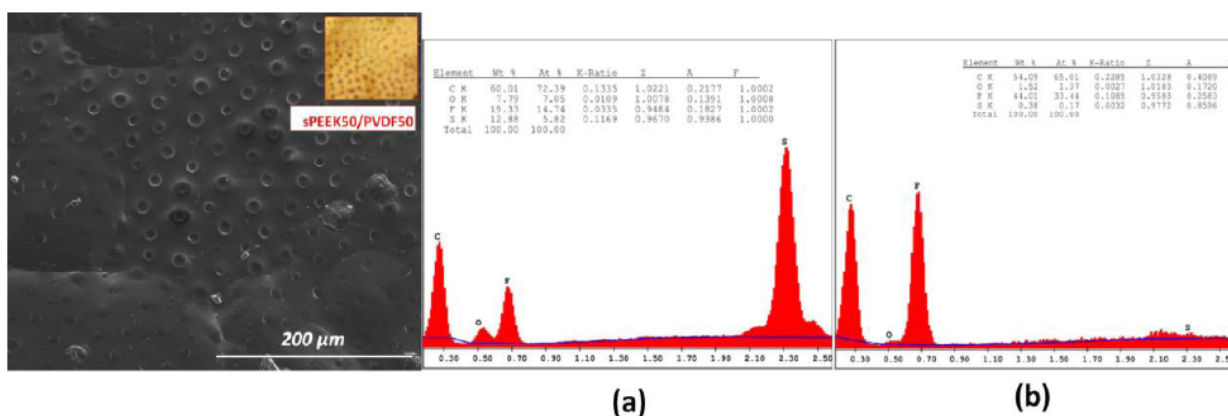


(c)

(d)

(e)

**Figure 5:** SEM pictures of (a) PVDF, (b) sPEEK, (c) sPEEK30/PVDF70, (d) sPEEK45/PVDF55 and (e) sPEEK50/PVDF50.



**Figure 6:** EDS graphs of (a) dark dots in sPEEK50/PVDF50 (upper right picture) and yellowish region in sPEEK50/PVDF50.

spherically disturbed phase was sulfur enriched region. This result indicated that the dark dots in the upper picture were attributed to the presence sulfonic acid groups and sPEEK (Figure.6a). The other main phase was corresponded to immensely fluorine-containing PVDF (Figure.6b).

## CONCLUSION

Five different blend membranes of sulfonated poly(ether ether ketone) (sPEEK) and poly(vinylidene fluoride) (PVDF) are prepared with various mixing volume ratios for direct methanol fuel cell (DMFC) applications. Furthermore, the effects of sPEEK content on water uptake, proton conductivity ( $\sigma$ ), methanol permeability ( $P_M$ ), membrane selectivity ( $\Phi$ ) and morphology of the blend membranes are investigated. Water uptake values of the blend membranes vary between 9-20% as a function of the blend composition. Similar to the water uptake property, proton conductivity and surface hydrophilicity of the samples increase with sPEEK. Since most proton-conducting membranes based on sulfonated aromatic polymers exhibit significant dimensional change by hydration, it is considered that the blend membranes with 30-50% of sPEEK seem to be suitable. In addition, it is found that methanol permeability of the blend membranes dramatically decreases with PVDF content and they are much lower than that of pure sPEEK whereas proton conductivities of these membranes are comparable to that of sPEEK. The blend membranes are dense and uniform when sPEEK volume ratio below than 30 %. Beyond this point, sPEEK is distributed spherically in PVDF and the blend membranes lose their mechanical integrity during the methanol permeation tests. Also, it is found that the thermal stabilities of all prepared membranes are

above 200°C, which is sufficiently high for use in DMFCs. Comparing to Nafion®117 reported in the literature,  $P_M$  of the blend membrane is 10 times lower than that of Nafion®117, whereas proton conductivities of the commercial membrane is much larger than that of sPEEK/PVDF blend membrane. Based on the results, it can be concluded that the sPEEK/PVDF blends can be considered as a candidate membrane for DMFC applications due to their controllable properties, cheapness and easy preparation.

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